

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : KYOCERA CORP

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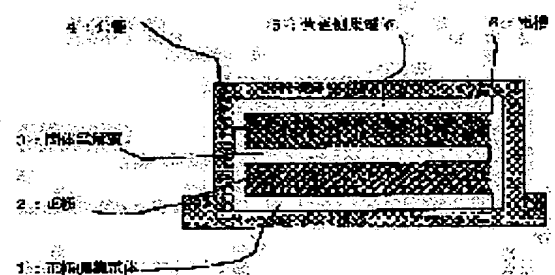
(72)Inventor : HARA TORU

(54) MANUFACTURING METHOD OF LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium secondary battery, that has high ion conductivity and a high energy density in the lithium secondary battery, of which the active material and solid electrolyte particles are bound by a binder.

SOLUTION: In the manufacturing method of a lithium secondary battery, in which a solid electrolyte having lithium ion conductivity is provided between the positive electrode and negative electrode composed of active material, capable of reversible occlusion and discharge of lithium ion, the particles of the active material and the solid electrolyte are first surface treated by tetraalkoxysilane, and then bound by a polymer of monoalkyltrialkoxysilane or a copolymer of monoalkyltrialkoxysilane and polydialkylsiloxane.



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CLAIMS

[Claim(s)]

[Claim 1]It is a manufacturing method of a lithium secondary battery which allocates a solid electrolyte which has lithium ion conductivity between positive and negative poles which consist of an active material in which reversible occlusion discharge of a lithium ion is possible, A manufacturing method of a lithium secondary battery characterized by binding with a monoalkyl trialkoxysilane polymer or a copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane after carrying out the surface treatment of the particles of said active material and a solid electrolyte by tetra alkoxysilane.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the lithium secondary battery which has improved the ion conductivity between the particles of an active material and a solid electrolyte, and the processability in a manufacturing process especially about the manufacturing method of the lithium secondary battery used for mobile computing devices, such as a notebook computer and a cellular phone.

[0002]

[Description of the Prior Art]Conventionally, the organic electrolysis liquid which dissolved lithium salt in the organic solvent is used for the electrolyte of the lithium secondary battery used as a power supply of mobile computing devices.

The liquid spill had become a problem.

Then, many trials which use a solid electrolyte instead of organic electrolysis liquid have been made.

[0003]One of the solid electrolytes has a solid polymer electrolyte of the salt yne type in which polyether was made to dissolve lithium salt. In a salt yne type solid polymer electrolyte, when a lithium ion carries out hopping of between the oxygen atoms which are hopping sites, ion conduction becomes possible. However, in a salt yne type solid polymer electrolyte, since the ion conduction of a counter ion occurred while the ion conduction of a lithium ion occurs, there was a problem that the transference number to lithium ion conduction became low.

[0004]On the other hand, as a solid electrolyte of the type which only a lithium ion contributes to ion conduction, 0. Sulfide system noncrystalline solid electrolytes, such as $0.1\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$, $\text{Li}_{1+x}\text{M}_x\text{Ti}_2-x(\text{PO}_4)_3$ [M has an inorganic solid electrolyte called oxide stock crystalline substance solid electrolytes, such as trivalent positive ion], such as aluminum. However, since an inorganic solid electrolyte was a brittle material, there was a problem that it was lacking in processability and slimming down was difficult.

[0005]Then, it is examined that it is compatible in high ionic conductivity and the outstanding processability by binding the particles of an inorganic solid electrolyte with the solid polymer electrolyte which has a hopping site to a lithium ion, and is not dissolving lithium salt. For example, in JP,10-3818,A, the solid electrolyte which mixed the polymer which makes it come to sulfonate a carbon-carbon double bond, and the particles of a sulfide system noncrystalline solid electrolyte or the particles of an oxide stock crystalline substance solid electrolyte is proposed. In such a solid electrolyte, the $-\text{SO}_3^-$ group which makes loose coordination a lithium ion electrically exists in the circumference of the point of contact when the particles of an inorganic solid electrolyte touch, It should excel also in processability, not barring ion conduction between particles, therefore maintaining the high ionic conductivity of an inorganic solid electrolyte, in order that this may carry a lithium ion by molecular motion. It is able to propose forming the electrode which furthermore bound the active material with JP,10-3926,A using the polymer sulfonated similarly, and to form a totally-solid lithium secondary battery combining the solid electrolyte of previous JP,10-3818,A.

[0006]

[Problem(s) to be Solved by the Invention]However, in the above totally-solid lithium secondary batteries, since the rubber elasticity of a polymer would be lost if a sulfonation rate is made high, processability fell, and since the hopping sites of a lithium ion would decrease in number if a sulfonation rate is conversely low, there was a problem that ionic conductivity fell. In such a case, since reservation of ionic conductivity is top priority, processability falls victim. For this reason, in JP,10-3818,A. The fall of processability needed to be compensated with using a mesh the product made from polyethylene, or glass as a supporter, and in order that the part

containing a supporter might reduce the fill ration of an active material or a solid electrolyte, there was a problem of bringing about the fall of an energy density.

[0007] This invention is made in view of the problem in the above-mentioned conventional technology, and the purpose is to improve processability, without reducing ion conductivity and to provide the highly efficient lithium secondary battery with easy handling also in the case of manufacture.

[0008]

[Means for Solving the Problem] A manufacturing method of a lithium secondary battery concerning claim 1 of this invention, It is a manufacturing method of a lithium secondary battery which allocates a solid electrolyte which has lithium ion conductivity between positive and negative poles which consist of an active material in which reversible occlusion discharge of a lithium ion is possible, It binds with a monoalkyl trialkoxysilane polymer or a copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane, after carrying out the surface treatment of the particles of said active material and a solid electrolyte by tetra alkoxy silane.

[0009] According to the manufacturing method of a lithium secondary battery of this invention, by carrying out the surface treatment of the particles of an active material and a solid electrolyte by tetra alkoxy silane, A result to which tetra alkoxy silane monomer also enters a detailed crevice of a particle surface, and a very narrow gap between particles, A hopping site will exist with high density and a capacity factor of an active material improves, By furthermore binding with a monoalkyl trialkoxysilane polymer or a copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane, Since a hopping site exists near the point of contact of particles of an active material and a solid electrolyte, Since a binder which can reduce resistance to ion conduction between particles, and also binds particles is rich in flexibility, Since it is not necessary to use supporters, such as a polyethylene mesh and a glass mesh, like before, therefore a fill ration of an active material can be increased and it becomes high energy density as a result, For example, when used as a power supply of mobile computing devices, a lithium secondary battery which can make apparatus drive for a long time can be produced.

[0010]

[Embodiment of the Invention] Hereafter, based on a drawing, this invention is explained in detail.

[0011] Drawing 1 is a sectional view showing an example of the lithium secondary battery produced by the manufacturing method of the lithium secondary battery of this invention. As for a solid electrolyte and 4, in drawing 1, the anode side charge collector and 2 are [the negative-electrode side charge collector and 6] battery cases a negative electrode and 5 an anode and 3 1.

[0012] As an active material used for the anode 2 and the negative electrode 4, A spinel type lithium manganese multiple oxide, a spinel type lithium magnesium manganese multiple oxide, At least one kind in a spinel type lithium-nickel-manganese multiple oxide, a spinel type lithium titanium multiple oxide, a spinel type lithium niobium titanium multiple oxide, and a spinel type lithium iron titanium multiple oxide is used. If these do not have anisotropy in order that the channel of a lithium ion may take the three-dimensional structure, therefore which field of a crystal exists in the point of contact between particles, since it is uninfluential to the ejection and insertion of a lithium ion, it is an active material suitable for the lithium secondary battery using a solid electrolyte. These active materials have a small volume change accompanying charge and discharge, therefore since the crystal collapse accompanying charge and discharge does not take place easily, they are active materials suitable for the lithium secondary battery using a solid electrolyte.

[0013] As a lithium-ion-conductivity crystalline substance oxide used for the solid electrolyte 3, $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ [M Trivalent positive ion], such as aluminum, $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ [M Trivalent positive ion], such as aluminum, When a univalent or divalent positive ion and M of $\text{Li}_{1+(4-n)x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ [M are univalent and n= 1 and M are divalent, as for n= 2 and x, at least one kind in 0.1 - 0.5] is used.

[0014] Tetra alkoxy silane is used as a finishing agent used for the surface treatment of the particles of positive active material, negative electrode active material, and a solid electrolyte. It mixes as the method of a surface treatment, stirring the particles and tetra alkoxy silane of an active material or a solid electrolyte, and the method of drying at the temperature of not less than 120 ** is used. After desiccation, tetra alkoxy silane united on the surface of particles remains, and the excessive tetra alkoxy silane which was not combined carries out decomposition evaporation. The result to which tetra alkoxy silane monomer also enters the inside of the detailed crevice of a particle surface, and the very narrow gap between particles by performing the surface treatment by tetra alkoxy silane, A hopping site will exist with high density, the capacity factor of an active material improves, since tetra alkoxy silane further united on the surface of particles has a binder and good compatibility, the hopping site included in a binder can draw near near the particles, and ionic conductivity improves.

[0015]As a binder which binds the particles of positive active material, negative electrode active material, and a solid electrolyte, a monoalkyl trialkoxysilane polymer or the copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane is used. Monoalkyl trialkoxysilane is used as a charge of a principal member which constitutes the three-dimensional structure which arranges the oxygen atom which is a hopping site with high density, and also is rich also in flexibility. Since it has the molecular structure of straight chain shape, a poly dialkyl siloxane is used in order to raise the flexibility of a copolymer.

[0016]The conducting agent and monoalkyl trialkoxysilane polymer which consist of charges of a conductive carbon material which carried out the surface treatment by tetra alkoxy silane, such as an active material and acetylene black, in order to produce the anode 2 or the negative electrode 4, Or the copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane is mixed, a slurry is adjusted, this slurry is applied to the anode side charge collector 1 or the negative-electrode side charge collector 5, and the method of hardening at 150-200 ** is used. Under the present circumstances, an about [1wt%] organotin compound may be added as a hardening accelerator. As such an organotin compound, dibutyldiacetoxytin etc. are used, for example.

[0017]The lithium-ion-conductivity crystalline substance oxide and monoalkyl trialkoxysilane polymer which carried out the surface treatment by tetra alkoxy silane in order to have produced the solid electrolyte 3, Or the copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane is mixed, a slurry is adjusted, this slurry is applied to the anode 2 and/or the negative electrode 4, and the method of hardening at 150-200 ** is used.

[0018]Aluminium foil etc. are used for the anode side charge collector 1 and the negative-electrode side charge collector 5.

[0019]A polyethylene terephthalate film, aluminium foil, the laminate film that laminated the polyethylene film, etc. are used for the battery case 6, for example.

[0020]

[Example]Next, an example is explained about the manufacturing method of the lithium secondary battery of this invention.

[0021][Example 1] First, by binding with a tetraethoxysilane the particles which carried out the surface treatment using a monomethyl trimethoxysilane polymer (average molecular weight 10000) / poly dimethylsiloxane (average molecular weight 1000) =80/20wt% copolymer, Lithium secondary battery A concerning the manufacturing method of the lithium secondary battery of this invention was produced.

[0022] $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ which is positive active material, $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ which is negative electrode active material, The surface treatment was performed by mixing with a tetraethoxysilane $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ which is a solid electrolyte, respectively, and drying at 120 ** for 2 hours.

[0023] $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ which performed the surface treatment 86wt%, the copolymer which consists of monomethyl trimethoxysilane / poly dimethylsiloxane (average molecular weight 1000) =80/20wt% acetylene black which is a conducting agent 9wt% -- 5wt% -- weighing was carried out, these were mixed and the slurry was adjusted.

[0024]Applied this slurry on aluminium foil, it was made to harden by heat-treating at 200 ** for 2 hours, and the anode was formed.

[0025] $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ which performed the surface treatment 86wt%, the copolymer which consists of monomethyl trimethoxysilane / poly dimethylsiloxane (average molecular weight 1000) =80/20wt% acetylene black which is a conducting agent 9wt% -- 5wt% -- weighing was carried out, these were mixed and the slurry was adjusted.

[0026]Applied this slurry on aluminium foil, it was made to harden by heat-treating at 200 ** for 2 hours, and the negative electrode was formed.

[0027] $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ which performed the surface treatment 95wt%, the copolymer which consists of monomethyl trimethoxysilane / poly dimethylsiloxane (average molecular weight 1000) =80/20wt% -- 5wt% -- weighing was carried out, these were mixed and the slurry was adjusted.

[0028]After applying this slurry to the anode and the negative electrode and pasting these together, it was made to harden by heat-treating at 200 ** for 2 hours, and the battery element was formed.

[0029]As for the size, the solid electrolyte set to 10 micrometers by the anode having set to 20 micrometers, and the negative electrode set 50x50 mm and thickness to 20 micrometers a total of 50 micrometers.

[0030]After carrying out vacuum drying of the battery element over 2 hours at 200 **, it wrapped in the aluminum polyethylene laminate film, and the battery case was formed by carrying out heating weld.

[0031]As a comparative example, it bound with the polymer which makes it come in the same active material

material as the above, and the same solid electrolyte materials as the above to sulfonate a carbon-carbon double bond, and lithium secondary battery B by the conventional method held and formed in a polyethylene mesh was produced.

[0032] And the charge-and-discharge capacitance characteristics of the positive-active-material standard were searched for with the current density of $100\text{microA}/\text{cm}^2$ using the charge-and-discharge measuring device about these lithium secondary batteries A and B. The result of these charge-and-discharge capacitance characteristics is shown in Table 1.

[0033]

[Table 1]

試料	正極活物質／負極活物質充填量 (mg)	充電／放電容量 (mAh)
リチウム二次電池A	255／235	27／26
リチウム二次電池B	154／142	16／13

[0034] Table 1 indicates charge-and-discharge capacitance characteristics to be a fill ration of the positive active material of lithium secondary battery A and lithium secondary battery B, and negative electrode active material. The fill ration of lithium secondary battery A of the active material is more than lithium secondary battery B, and it has good charge-and-discharge capacitance characteristics so that these may show.

[0035] After carrying out the surface treatment of the particles of the active material of this invention, and a solid electrolyte by tetra alkoxysilane by this, Since the binder which binds particles is rich in flexibility, the lithium secondary battery bound with the monoalkyl trialkoxysilane polymer or the copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane is the copolymer in which molecular motion was activated.

Can reduce the resistance to the ion conduction between particles in such a binder existing near the point of contact of the particles of an active material and a solid electrolyte, since it has a hopping site with high density, and also [and]. Since the fill ration of an active material can be increased by using supporters, such as a polyethylene mesh and a glass mesh, like before as compared with that with which the fall of processability is compensated and it becomes high energy density as a result, it becomes a lithium secondary battery which has good charge-and-discharge capacitance characteristics.

[0036]

[Effect of the Invention] As mentioned above, after carrying out the surface treatment of the particles of an active material and a solid electrolyte by tetra alkoxysilane in this invention, By binding with a monoalkyl trialkoxysilane polymer or the copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane, The result to which tetra alkoxysilane monomer also enters the inside of the detailed crevice of a particle surface, and the very narrow gap between particles, A hopping site will exist with high density and the capacity factor of an active material improves, Since the hopping site which is furthermore in a monoalkyl trialkoxysilane polymer or the copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane exists near the point of contact of the particles of an active material and a solid electrolyte, Since the binder which can reduce the resistance to the ion conduction between particles, and also binds particles is rich in flexibility, As compared with that with which the fall of processability is compensated, the fill ration of an active material can be increased by using supporters, such as a polyethylene mesh and a glass mesh, like before, and, as a result, it becomes high energy density.

Therefore, the lithium secondary battery which has a good battery characteristic can be provided.

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TECHNICAL FIELD

[Field of the Invention]This invention relates to the manufacturing method of the lithium secondary battery which has improved the ion conductivity between the particles of an active material and a solid electrolyte, and the processability in a manufacturing process especially about the manufacturing method of the lithium secondary battery used for mobile computing devices, such as a notebook computer and a cellular phone.

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PRIOR ART

[Description of the Prior Art]Conventionally, the organic electrolysis liquid which dissolved lithium salt in the organic solvent is used for the electrolyte of the lithium secondary battery used as a power supply of mobile computing devices.

The liquid spill had become a problem.

Then, many trials which use a solid electrolyte instead of organic electrolysis liquid have been made.

[0003]One of the solid electrolytes has a solid polymer electrolyte of the salt yne type in which polyether was made to dissolve lithium salt. In a salt yne type solid polymer electrolyte, when a lithium ion carries out hopping of between the oxygen atoms which are hopping sites, ion conduction becomes possible. However, in a salt yne type solid polymer electrolyte, since the ion conduction of a counter ion occurred while the ion conduction of a lithium ion occurs, there was a problem that the transference number to lithium ion conduction became low.

[0004]On the other hand, as a solid electrolyte of the type which only a lithium ion contributes to ion conduction, 0. Sulfide system noncrystalline solid electrolytes, such as $0.1\text{Li}_3\text{PO}_4-0.63\text{Li}_2\text{S}-0.36\text{SiS}_2$, $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ [M has an inorganic solid electrolyte called oxide stock crystalline substance solid electrolytes, such as trivalent positive ion], such as aluminum. However, since an inorganic solid electrolyte was a brittle material, there was a problem that it was lacking in processability and slimming down was difficult.

[0005]Then, it is examined that it is compatible in high ionic conductivity and the outstanding processability by binding the particles of an inorganic solid electrolyte with the solid polymer electrolyte which has a hopping site to a lithium ion, and is not dissolving lithium salt. For example, in JP,10-3818,A, the solid electrolyte which mixed the polymer which makes it come to sulfonate a carbon-carbon double bond, and the particles of a sulfide system noncrystalline solid electrolyte or the particles of an oxide stock crystalline substance solid electrolyte is proposed. In such a solid electrolyte, the $-\text{SO}_3^-$ group which makes loose coordination a lithium ion electrically exists in the circumference of the point of contact when the particles of an inorganic solid electrolyte touch. It should excel also in processability, not barring ion conduction between particles, therefore maintaining the high ionic conductivity of an inorganic solid electrolyte, in order that this may carry a lithium ion by molecular motion. It is able to propose forming the electrode which furthermore bound the active material with JP,10-3926,A using the polymer sulfonated similarly, and to form a totally-solid lithium secondary battery combining the solid electrolyte of previous JP,10-3818,A.

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EFFECT OF THE INVENTION

[Effect of the Invention]As mentioned above, after carrying out the surface treatment of the particles of an active material and a solid electrolyte by tetra alkoxysilane in this invention, By binding with a monoalkyl trialkoxysilane polymer or the copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane, The result to which tetra alkoxysilane monomer also enters the inside of the detailed crevice of a particle surface, and the very narrow gap between particles, A hopping site will exist with high density and the capacity factor of an active material improves, Since the hopping site which is furthermore in a monoalkyl trialkoxysilane polymer or the copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane exists near the point of contact of the particles of an active material and a solid electrolyte, Since the binder which can reduce the resistance to the ion conduction between particles, and also binds particles is rich in flexibility, As compared with that with which the fall of processability is compensated, the fill ration of an active material can be increased by using supporters, such as a polyethylene mesh and a glass mesh, like before, and, as a result, it becomes high energy density.

Therefore, the lithium secondary battery which has a good battery characteristic can be provided.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]However, in the above totally-solid lithium secondary batteries, since the rubber elasticity of a polymer would be lost if a sulfonation rate is made high, processability fell, and since the hopping sites of a lithium ion would decrease in number if a sulfonation rate is conversely low, there was a problem that ionic conductivity fell. In such a case, since reservation of ionic conductivity is top priority, processability falls victim. For this reason, in JP,10-3818,A. The fall of processability needed to be compensated with using a mesh the product made from polyethylene, or glass as a supporter, and in order that the part containing a supporter might reduce the fill ration of an active material or a solid electrolyte, there was a problem of bringing about the fall of an energy density.

[0007]This invention is made in view of the problem in the above-mentioned conventional technology, and the purpose is to improve processability, without reducing ion conductivity and to provide the highly efficient lithium secondary battery with easy handling also in the case of manufacture.

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MEANS

[Means for Solving the Problem]A manufacturing method of a lithium secondary battery concerning claim 1 of this invention, It is a manufacturing method of a lithium secondary battery which allocates a solid electrolyte which has lithium ion conductivity between positive and negative poles which consist of an active material in which reversible occlusion discharge of a lithium ion is possible, It binds with a monoalkyl trialkoxysilane polymer or a copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane, after carrying out the surface treatment of the particles of said active material and a solid electrolyte by tetra alkoxysilane.

[0009]According to the manufacturing method of a lithium secondary battery of this invention, by carrying out the surface treatment of the particles of an active material and a solid electrolyte by tetra alkoxysilane, A result to which tetra alkoxysilane monomer also enters a detailed crevice of a particle surface, and a very narrow gap between particles, A hopping site will exist with high density and a capacity factor of an active material improves, By furthermore binding with a monoalkyl trialkoxysilane polymer or a copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane, Since a hopping site exists near the point of contact of particles of an active material and a solid electrolyte, Since a binder which can reduce resistance to ion conduction between particles, and also binds particles is rich in flexibility, Since it is not necessary to use supporters, such as a polyethylene mesh and a glass mesh, like before, therefore a fill ration of an active material can be increased and it becomes high energy density as a result, For example, when used as a power supply of mobile computing devices, a lithium secondary battery which can make apparatus drive for a long time can be produced.

[0010]

[Embodiment of the Invention]Hereafter, based on a drawing, this invention is explained in detail.

[0011]Drawing 1 is a sectional view showing an example of the lithium secondary battery produced by the manufacturing method of the lithium secondary battery of this invention. As for a solid electrolyte and 4, in drawing 1, the anode side charge collector and 2 are [the negative-electrode side charge collector and 6] battery cases a negative electrode and 5 an anode and 3 1.

[0012]As an active material used for the anode 2 and the negative electrode 4, A spinel type lithium manganese multiple oxide, a spinel type lithium magnesium manganese multiple oxide, At least one kind in a spinel type lithium-nickel-manganese multiple oxide, a spinel type lithium titanium multiple oxide, a spinel type lithium niobium titanium multiple oxide, and a spinel type lithium iron titanium multiple oxide is used. If these do not have anisotropy in order that the channel of a lithium ion may take the three-dimensional structure, therefore which field of a crystal exists in the point of contact between particles, since it is uninfluent to the ejection and insertion of a lithium ion, it is an active material suitable for the lithium secondary battery using a solid electrolyte. These active materials have a small volume change accompanying charge and discharge, therefore since the crystal collapse accompanying charge and discharge does not take place easily, they are active materials suitable for the lithium secondary battery using a solid electrolyte.

[0013]As a lithium-ion-conductivity crystalline substance oxide used for the solid electrolyte 3, $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ [M Trivalent positive ion], such as aluminum, $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ [M Trivalent positive ion], such as aluminum, When a univalent or divalent positive ion and M of $\text{Li}_{1+(4-n)x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ [M are univalent and $n=1$ and M are divalent, as for $n=2$ and x, at least one kind in 0.1 - 0.5] is used.

[0014]Tetra alkoxysilane is used as a finishing agent used for the surface treatment of the particles of positive active material, negative electrode active material, and a solid electrolyte. It mixes as the method of a surface treatment, stirring the particles and tetra alkoxysilane of an active material or a solid electrolyte, and the method of drying at the temperature of not less than 120 ** is used. After desiccation, tetra alkoxysilane united on the

surface of particles remains, and the excessive tetra alkoxysilane which was not combined carries out decomposition evaporation. The result to which tetra alkoxysilane monomer also enters the inside of the detailed crevice of a particle surface, and the very narrow gap between particles by performing the surface treatment by tetra alkoxysilane, A hopping site will exist with high density, the capacity factor of an active material improves, since tetra alkoxysilane further united on the surface of particles has a binder and good compatibility, the hopping site included in a binder can draw near near the particles, and ionic conductivity improves.

[0015]As a binder which binds the particles of positive active material, negative electrode active material, and a solid electrolyte, a monoalkyl trialkoxysilane polymer or the copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane is used. Monoalkyl trialkoxysilane is used as a charge of a principal member which constitutes the three-dimensional structure which arranges the oxygen atom which is a hopping site with high density, and also is rich also in flexibility. Since it has the molecular structure of straight chain shape, a poly dialkyl siloxane is used in order to raise the flexibility of a copolymer.

[0016]The conducting agent and monoalkyl trialkoxysilane polymer which consist of charges of a conductive carbon material which carried out the surface treatment by tetra alkoxysilane, such as an active material and acetylene black, in order to produce the anode 2 or the negative electrode 4, Or the copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane is mixed, a slurry is adjusted, this slurry is applied to the anode side charge collector 1 or the negative-electrode side charge collector 5, and the method of hardening at 150-200 ** is used. Under the present circumstances, an about [1wt%] organotin compound may be added as a hardening accelerator. As such an organotin compound, dibutyldiacetoxytin etc. are used, for example.

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[0018]Aluminium foil etc. are used for the anode side charge collector 1 and the negative-electrode side charge collector 5.

[0019]A polyethylene terephthalate film, aluminium foil, the laminate film that laminated the polyethylene film, etc. are used for the battery case 6, for example.

[Translation done.]

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EXAMPLE

[Example]Next, an example is explained about the manufacturing method of the lithium secondary battery of this invention.

[0021][Example 1] First, by binding with a tetraethoxysilane the particles which carried out the surface treatment using a monomethyl trimethoxysilane polymer (average molecular weight 10000) / poly dimethylsiloxane (average molecular weight 1000) =80/20wt% copolymer, Lithium secondary battery A concerning the manufacturing method of the lithium secondary battery of this invention was produced.

[0022] $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ which is positive active material, $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ which is negative electrode active material, The surface treatment was performed by mixing with a tetraethoxysilane $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ which is a solid electrolyte, respectively, and drying at 120 ** for 2 hours.

[0023] $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ which performed the surface treatment 86wt%, the copolymer which consists of monomethyl trimethoxysilane / poly dimethylsiloxane (average molecular weight 1000) =80/20wt% acetylene black which is a conducting agent 9wt% -- 5wt% -- weighing was carried out, these were mixed and the slurry was adjusted.

[0024]Applied this slurry on aluminium foil, it was made to harden by heat-treating at 200 ** for 2 hours, and the anode was formed.

[0025] $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ which performed the surface treatment 86wt%, the copolymer which consists of monomethyl trimethoxysilane / poly dimethylsiloxane (average molecular weight 1000) =80/20wt% acetylene black which is a conducting agent 9wt% -- 5wt% -- weighing was carried out, these were mixed and the slurry was adjusted.

[0026]Applied this slurry on aluminium foil, it was made to harden by heat-treating at 200 ** for 2 hours, and the negative electrode was formed.

[0027] $\text{Li}_{1.3}\text{aluminum}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ which performed the surface treatment 95wt%, the copolymer which consists of monomethyl trimethoxysilane / poly dimethylsiloxane (average molecular weight 1000) =80/20wt% -- 5wt% -- weighing was carried out, these were mixed and the slurry was adjusted.

[0028]After applying this slurry to the anode and the negative electrode and pasting these together, it was made to harden by heat-treating at 200 ** for 2 hours, and the battery element was formed.

[0029]As for the size, the solid electrolyte set to 10 micrometers by the anode having set to 20 micrometers, and the negative electrode set 50x50 mm and thickness to 20 micrometers a total of 50 micrometers.

[0030]After carrying out vacuum drying of the battery element over 2 hours at 200 **, it wrapped in the aluminum polyethylene laminate film, and the battery case was formed by carrying out heating weld.

[0031]As a comparative example, it bound with the polymer which makes it come in the same active material material as the above, and the same solid electrolyte materials as the above to sulfonate a carbon-carbon double bond, and lithium secondary battery B by the conventional method held and formed in a polyethylene mesh was produced.

[0032]And the charge-and-discharge capacitance characteristics of the positive-active-material standard were searched for with the current density of $100\text{microA}/\text{cm}^2$ using the charge-and-discharge measuring device about these lithium secondary batteries A and B. The result of these charge-and-discharge capacitance characteristics is shown in Table 1.

[0033]

[Table 1]

試料	正極活物質／負極活物質充填量 (m g)	充電／放電容量 (m A h)
リチウム二次電池A	2 5 5 ／ 2 3 5	2 7 ／ 2 6
リチウム二次電池B	1 5 4 ／ 1 4 2	1 6 ／ 1 3

[0034]Table 1 indicates charge-and-discharge capacitance characteristics to be a fill ration of the positive active material of lithium secondary battery A and lithium secondary battery B, and negative electrode active material. The fill ration of lithium secondary battery A of the active material is more than lithium secondary battery B, and it has good charge-and-discharge capacitance characteristics so that these may show.

[0035]After carrying out the surface treatment of the particles of the active material of this invention, and a solid electrolyte by tetra alkoxysilane by this, Since the binder which binds particles is rich in flexibility, the lithium secondary battery bound with the monoalkyl trialkoxysilane polymer or the copolymer of monoalkyl trialkoxysilane and a poly dialkyl siloxane is the copolymer in which molecular motion was activated.

Can reduce the resistance to the ion conduction between particles in such a binder existing near the point of contact of the particles of an active material and a solid electrolyte, since it has a hopping site with high density, and also [and]. Since the fill ration of an active material can be increased by using supporters, such as a polyethylene mesh and a glass mesh, like before as compared with that with which the fall of processability is compensated and it becomes high energy density as a result, it becomes a lithium secondary battery which has good charge-and-discharge capacitance characteristics.

[0036]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a sectional view showing an example of the embodiment of the lithium secondary battery produced by the manufacturing method of the lithium secondary battery of this invention.

[Description of Notations]

1: The anode side charge collector, 2:anode, 3:solid electrolyte, and 4:negative-electrode side and 5:negative-electrode side charge collector, 6 : battery case

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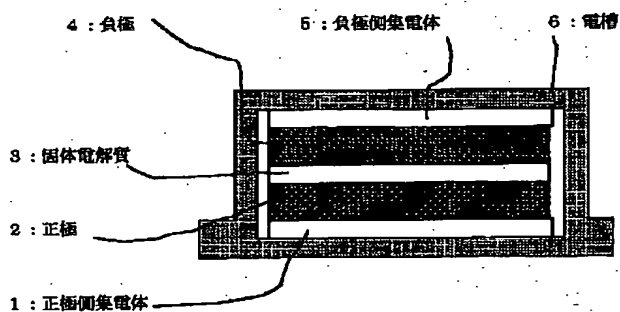
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DRAWINGS

[Drawing 1]



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(71)出願人 000006633

京セラ株式会社

京都府京都市伏見区竹田烏羽殿町6番地

(72)発明者 原 亨

京都府相楽郡精華町光台3丁目5番地 京

セラ株式会社中央研究所内

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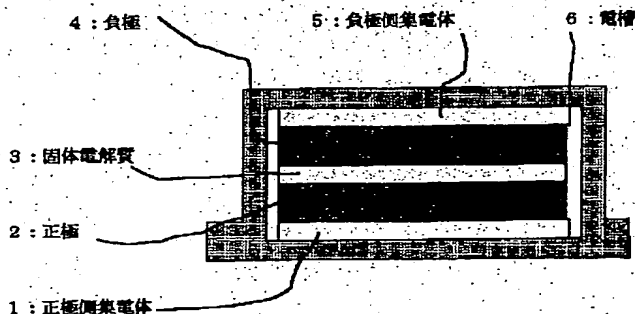
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(54)【発明の名称】 リチウム二次電池の製造方法

(57)【要約】

【課題】 活物質および固体電解質の粒子を結着剤で結着したリチウム二次電池において、イオン伝導度が高く、エネルギー密度が高いリチウム二次電池を提供する。

【解決手段】 リチウムイオンの可逆的な吸蔵放出が可能な活物質からなる正負極間にリチウムイオン伝導性を有する固体電解質を配設してなるリチウム二次電池の製造方法において、活物質および固体電解質の粒子をテトラアルコキシシランで表面処理した後、モノアルキルトリアルコキシシラン重合体、またはモノアルキルトリアルコキシシランとポリジアルキルシロキサンとの共重合体で結着する。



【特許請求の範囲】

【請求項1】 リチウムイオンの可逆的な吸蔵放出が可能な活物質からなる正負極間にリチウムイオン伝導性を有する固体電解質を配設してなるリチウム二次電池の製造方法であって、前記活物質および固体電解質の粒子をテトラアルコキシシランで表面処理した後、モノアルキルトリアルコキシシラン重合体、またはモノアルキルトリアルコキシシランとポリジアルキルシロキサンとの共重合体で結着することを特徴とするリチウム二次電池の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明はノートパソコンや携帯電話等のモバイル機器に使用されるリチウム二次電池の製造方法に関し、特に活物質および固体電解質の粒子間のイオン伝導性と製造過程における加工性を改善したリチウム二次電池の製造方法に関する。

【0002】

【従来の技術】 従来、モバイル機器の電源として用いられるリチウム二次電池の電解質には、リチウム塩を有機溶媒に溶解した有機電解液が用いられており、漏液が問題となっていた。そこで、有機電解液の代わりに固体電解質を用いる試みが多数なされてきた。

【0003】 固体電解質の一つに、ポリエーテルにリチウム塩を溶解させたソルトインタイプの高分子固体電解質がある。ソルトインタイプの高分子固体電解質では、ホッピングサイトである酸素原子の間をリチウムイオンがホッピングすることによりイオン伝導が可能となる。しかしながら、ソルトインタイプの高分子固体電解質では、リチウムイオンのイオン伝導があると同時に、対イオンのイオン伝導があるため、リチウムイオン伝導に対する輸率が低くなるという問題があった。

【0004】 一方、リチウムイオンのみがイオン伝導に寄与するタイプの固体電解質として、 $0.01Li_3PO_4-0.63Li_2S-0.36SiS_2$ などの硫化物系非晶質固体電解質や、 $Li_{1-x}M_xTi_{2-x}(PO_4)_3$ [MはAlなどの3価の陽イオン] などの酸化物系結晶質固体電解質といった無機固体電解質がある。しかしながら、無機固体電解質は脆性材料であるため、加工性に乏しく、薄型化が困難であるという問題があった。

【0005】 そこで、リチウムイオンに対するホッピングサイトを有し、かつリチウム塩を溶解していない高分子固体電解質で無機固体電解質の粒子を結着することで、高いイオン伝導度と優れた加工性を両立することが検討されている。例えば特開平10-3818号公報では、炭素-炭素二重結合をスルホン化させてなる重合体と、硫化物系非晶質固体電解質の粒子または酸化物系結晶質固体電解質の粒子とを混合した固体電解質を提案している。このような固体電解質では、無機固体電解質の粒子同士が接触している接触点の周囲にリチウムイオン

に電気的に緩い配位をする $-SO_3^-$ 基が存在し、これが分子運動によってリチウムイオンを運ぶため粒子間のイオン伝導を妨げることがなく、したがって無機固体電解質の高いイオン伝導度を維持したまま、加工性にも優れたものとして行うことができる。さらに特開平10-3926号公報では、同様にスルホン化した重合体を用いて活物質を結着した電極を形成することが提案されており、先の特開平10-3818号公報の固体電解質と組み合わせ、全固体リチウム二次電池を形成することが可能である。

【0006】

【発明が解決しようとする課題】 しかしながら、上記のような全固体リチウム二次電池においては、スルホン化率を高くすると重合体のゴム弾性が失われるため加工性が低下し、逆にスルホン化率が低いとリチウムイオンのホッピングサイトが減るため、イオン伝導度が低下するという問題があった。このような場合、イオン伝導度の確保が最優先であるため、加工性が犠牲になる。このため、特開平10-3818号公報では、ポリエチレン製またはガラス製のメッシュを保持体として用いることで加工性の低下を補う必要があり、保持体を含む分は活物質や固体電解質の充填量を減らすことになるため、エネルギー密度の低下をもたらすという問題点があった。

【0007】 本発明は上記従来技術における問題点に鑑みてなされたものであり、その目的は、イオン伝導性を低下させることなく加工性を改善して、高性能でかつ製造の際にも取り扱いの容易なリチウム二次電池を提供することにある。

【0008】

【課題を解決するための手段】 本発明の請求項1に係るリチウム二次電池の製造方法は、リチウムイオンの可逆的な吸蔵放出が可能な活物質からなる正負極間にリチウムイオン伝導性を有する固体電解質を配設してなるリチウム二次電池の製造方法であって、前記活物質および固体電解質の粒子をテトラアルコキシシランで表面処理した後、モノアルキルトリアルコキシシラン重合体、またはモノアルキルトリアルコキシシランとポリジアルキルシロキサンの共重合体で結着することを特徴とするものである。

【0009】 本発明のリチウム二次電池の製造方法によれば、活物質および固体電解質の粒子をテトラアルコキシシランで表面処理することにより、テトラアルコキシシランモノマーが粒子表面の微細な凹部や粒子間のごく狭い間隙にも入り込む結果、ホッピングサイトが高密度に存在することになり、活物質の利用率が向上し、さらにモノアルキルトリアルコキシシラン重合体、またはモノアルキルトリアルコキシシランとポリジアルキルシロキサンの共重合体で結着することにより、ホッピングサイトが活物質および固体電解質の粒子の接触点近傍に存在するため、粒子間のイオン伝導に対する抵抗を低減

できる上に、粒子を結着する結着剤が可撓性に富むため、従来のようにポリエチレンメッシュやガラスメッシュなどの保持体を用いる必要がなく、したがって活物質の充填量を多くすることができ、その結果高エネルギー密度となるので、例えばモバイル機器の電源として使用される場合には、機器を長時間駆動させることができるリチウム二次電池を作製することができる。

【0010】

【発明の実施の形態】以下、図面に基づいて本発明を詳細に説明する。

【0011】図1は本発明のリチウム二次電池の製造方法により作製されたリチウム二次電池の一例を示す断面図である。図1において、1は正極側集電体、2は正極、3は固体電解質、4は負極、5は負極側集電体、6は電槽である。

【0012】正極2および負極4に用いる活物質としては、スピネル型リチウムマンガン複合酸化物、スピネル型リチウムマグネシウムマンガン複合酸化物、スピネル型リチウムニッケルマンガン複合酸化物、スピネル型リチウムチタン複合酸化物、スピネル型リチウムニオブチタン複合酸化物、およびスピネル型リチウム鉄チタン複合酸化物のうちの少なくとも1種類が用いられる。これらはリチウムイオンのチャネルが3次元構造をとるため異方性が無く、したがって結晶のどの面が粒子間の接触点に存在しようとしリチウムイオンの脱挿入に影響はないことから、固体電解質を用いるリチウム二次電池に適した活物質である。またこれら活物質は充放電に伴う体積変化が小さく、したがって充放電に伴う結晶崩壊が起こりにくいため、固体電解質を用いるリチウム二次電池に適した活物質である。

【0013】固体電解質3に用いられるリチウムイオン伝導性結晶質酸化物としては、 $Li_{1-x} M_x Ti_{2-x} (PO_4)$ 、 $[MはAlなどの3価の陽イオン]$ 、 $Li_{1-3x} M_x Ti_{2-x} Si_y P_{3-y} O_{12}$ 、 $[MはAlなどの3価の陽イオン]$ 、 $Li_{1-(4-n)x} M_x Ti_{2-x} (PO_4)_3$ 、 $[Mは1価または2価の陽イオン、Mが1価のとき $n=1$ 、Mが2価のとき $n=2$ 、 $xは0.1\sim0.5$]$ のうちの少なくとも1種類が用いられる。

【0014】正極活物質、負極活物質、および固体電解質の粒子の表面処理に用いられる表面処理剤としては、テトラアルコキシシランが用いられる。表面処理の方法としては、活物質または固体電解質の粒子とテトラアルコキシシランとを攪拌しながら混合し、120℃以上の温度で乾燥する方法が用いられる。乾燥後には、粒子の表面に結合したテトラアルコキシシランが残留し、結合しなかった余分なテトラアルコキシシランは分解蒸発する。テトラアルコキシシランによる表面処理を施すことでテトラアルコキシシランモノマーが粒子表面の微細な凹部の中や粒子間のごく狭い間隙にも入り込む結果、ホッピングサイトが高密度に存在することになり、活物質

の利用率が向上し、さらに粒子の表面に結合したテトラアルコキシシランが結着剤と良好な親和性を有するため、結着剤中に含まれるホッピングサイトが粒子の近傍に引き寄せられ、イオン伝導度が向上する。

【0015】正極活物質、負極活物質、および固体電解質の粒子を結着する結着剤としてはモノアルキルトリアルコキシシラン重合体、またはモノアルキルトリアルコキシシランとポリジアルキルシロキサンとの共重合体を用いられる。モノアルキルトリアルコキシシランは、ホッピングサイトである酸素原子を高密度に配置させる上に可撓性にも富む三次元構造を構成する主材料として用いられる。ポリジアルキルシロキサンは直鎖状の分子構造を有するため、共重合体の可撓性を向上させるために用いられる。

【0016】正極2または負極4を作製するには、テトラアルコキシシランで表面処理した活物質とアセチレンブラックなどの導電性炭素材料からなる導電剤とモノアルキルトリアルコキシシラン重合体、またはモノアルキルトリアルコキシシランとポリジアルキルシロキサンとの共重合体とを混合してスラリーを調整し、このスラリーを正極側集電体1または負極側集電体5に塗布し、150～200℃で硬化する方法が用いられる。この際、硬化促進剤として1wt%程度の有機スズ化合物を添加してもよい。そのような有機スズ化合物としては、例えばジブチルジアセトキシルスズなどが用いられる。

【0017】固体電解質3を作製するには、テトラアルコキシシランで表面処理したリチウムイオン伝導性結晶質酸化物とモノアルキルトリアルコキシシラン重合体、またはモノアルキルトリアルコキシシランとポリジアルキルシロキサンとの共重合体とを混合してスラリーを調整し、このスラリーを正極2および/または負極4に塗布し、150～200℃で硬化する方法が用いられる。

【0018】正極側集電体1および負極側集電体5には、アルミニウム箔などが用いられる。

【0019】電槽6には、例えばポリエチレンテレフタレートフィルム、アルミニウム箔、およびポリエチレンフィルムを積層したラミネートフィルムなどが用いられる。

【0020】

【実施例】次に、本発明のリチウム二次電池の製造方法について具体例を説明する。

【0021】【例1】まず、テトラエトキシシランで表面処理した粒子をモノメチルトリメトキシシラン重合体（平均分子量10000）／ポリジメチルシロキサン（平均分子量1000）＝80／20wt%共重合体を用いて結着することにより、本発明のリチウム二次電池の製造方法に係るリチウム二次電池Aを作製した。

【0022】正極活物質である $Li_{1.1} Mn_{1.9} O_4$ 、負極活物質である $Li_{1.3} Mn_{1.7} O_4$ 、固体電解質である $Li_{1.3} Al_{0.3} Ti_{1.7} (PO_4)_3$ をそれぞれテトラ

エトキシシランと混合して、120℃で2時間乾燥することにより、表面処理を行った。

【0023】表面処理を行った $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ を86wt%、導電剤であるアセチレンブラックを9wt%、モノメチルトリメトキシシラン/ポリジメチルシロキサン(平均分子量1000)=80/20wt%からなる共重合体を5wt%秤量し、これらを混合してスラリーを調整した。

【0024】このスラリーをアルミニウム箔上に塗布し、200℃で2時間熱処理することにより硬化させて正極を形成した。

【0025】表面処理を行った $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ を86wt%、導電剤であるアセチレンブラックを9wt%、モノメチルトリメトキシシラン/ポリジメチルシロキサン(平均分子量1000)=80/20wt%からなる共重合体を5wt%秤量し、これらを混合してスラリーを調整した。

【0026】このスラリーをアルミニウム箔上に塗布し、200℃で2時間熱処理することにより硬化させて負極を形成した。

【0027】表面処理を行った $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ を95wt%、モノメチルトリメトキシシラン/ポリジメチルシロキサン(平均分子量1000)=*

*80/20wt%からなる共重合体を5wt%秤量し、これらを混合してスラリーを調整した。

【0028】このスラリーを正極および負極に塗布して、これらを張り合わせた後、200℃で2時間熱処理することにより硬化させて電池素子を形成した。

【0029】寸法は50×50mm、厚さは正極が20μm、固体電解質が10μm、負極が20μmの、計50μmとした。

【0030】電池素子を200℃で2時間かけて真空乾燥した後、アルミニウム-ポリエチレン・ラミネートフィルムで包んで、加熱融着することで電槽を形成した。

【0031】また、比較例として、上記と同じ活物質材料、上記と同じ固体電解質材料において、炭素-炭素二重結合をスルホン化させてなる重合体で結着し、ポリエチレンメッシュで保持して形成した従来法によるリチウム二次電池Bを作製した。

【0032】そして、これらリチウム二次電池A及びBについて正極活物質基準の充放電容量特性を充放電測定装置を用いて100μA/cm²の電流密度で求めた。

これらの充放電容量特性の結果を表1に示す。

【0033】

【表1】

試料	正極活物質/負極活物質充填量 (mg)	充電/放電容量 (mAh)
リチウム二次電池A	255/235	27/26
リチウム二次電池B	154/142	16/13

【0034】表1はリチウム二次電池Aとリチウム二次電池Bの正極活物質および負極活物質の充填量と、充放電容量特性を示すものである。これらから分かるようにリチウム二次電池Aのほうがリチウム二次電池Bよりも活物質の充填量が多くなっており、良好な充放電容量特性を有している。

【0035】これにより、本発明の活物質および固体電解質の粒子をテトラアルコキシシランで表面処理した後、モノアルキルトリアルコキシシラン重合体、またはモノアルキルトリアルコキシシランとポリジアルキルシロキサンとの共重合体で結着したリチウム二次電池は、粒子を結着する結着剤が可撓性に富むため、分子運動が活性化された共重合体であり、しかもホッピングサイトを高密度に有することから、このような結着剤が活物質および固体電解質の粒子の接触点近傍に存在することで粒子間のイオン伝導に対する抵抗を低減できる上に、従来のようにポリエチレンメッシュやガラスメッシュなどの保持体を用いることで加工性の低下を補うものと比較して活物質の充填量を多くすることができ、その結果高エネルギー密度となるので、良好な充放電容量特性を有するリチウム二次電池となる。

【0036】

【発明の効果】以上のように、本発明によれば、活物質および固体電解質の粒子をテトラアルコキシシランで表面処理した後、モノアルキルトリアルコキシシラン重合体、またはモノアルキルトリアルコキシシランとポリジアルキルシロキサンとの共重合体で結着することにより、テトラアルコキシシランモノマーが粒子表面の微細な凹部の中や粒子間のごく狭い間隙にも入り込む結果、ホッピングサイトが高密度に存在することになり、活物質の利用率が向上し、さらにモノアルキルトリアルコキシシラン重合体、またはモノアルキルトリアルコキシシランとポリジアルキルシロキサンとの共重合体中にあるホッピングサイトが活物質および固体電解質の粒子の接触点近傍に存在するため、粒子間のイオン伝導に対する抵抗を低減できる上に、粒子を結着する結着剤が可撓性に富むため、従来のようにポリエチレンメッシュやガラスメッシュなどの保持体を用いることで加工性の低下を補うものと比較して、活物質の充填量を多くすることができ、その結果高エネルギー密度となるので、良好な電池特性を有するリチウム二次電池を提供することができる。

【図面の簡単な説明】

【図1】本発明のリチウム二次電池の製造方法により作

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製されたりチウム二次電池の実施の形態の一例を示す断面図である。

【符号の説明】

* 1：正極側集電体、2：正極、3：固体電解質、4：負極、5：負極側集電体、6：電槽

*

【図1】

